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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

#8/jm  
05/11/03

In re the application of:

WAKI, MINORU

Group Art Unit: 1714

Serial Number: 09/916,316

Examiner: Callie E. Shosho

Filed: July 30, 2001

For: WATER-BASED INK COMPOSITION FOR INK-JET PRINTING, INK-JET PRINTING METHOD USING THE SAME AND PRINTED MATTER

DECLARATION UNDER 37 CFR 1.132

Honorable Commissioner

**GROUP 1700**

Washington, D.C. 20231

APR 30 2003

**RECEIVED**

Sir,

We, Kazuaki Watanabe and Minoru Waki, the inventors residing at c/o SEIKO EPSON CORPORATION, 3-5, Owa 3-chome, Suwa-shi, NAGANO, JAPAN and c/o MIKUNI SHIKISO KABUSHIKI KAISHA, 101, Kokubunji, Mikunino-cho, Himeji-shi, HYOGO, JAPAN duly depose and say:

1. That Kazuaki Watanabe received the degree of master from Department of Engineering Science, Osaka University, Japan in the year 1987, and MINORU WAKI graduated from Himeji Institute of Technology, Japan in the year 1978;

2. That Kazuaki Watanabe has been employed in SEIKO EPSON CORPORATION since 1987, and WAKI MINORU has been employed in MIKUNI SHIKISO KABUSHIKI KAISHA since 1978;

3. That Kazuaki Watanabe has been engaged in TP Research and Development department from 1992, and WAKI MINORU

has been engaged in research and development;

4. That we have read and are familiar with the instant application for United States Letters Patent and Office Action thereto mailed January 15, 2003; and

5. That we have made experiments in order to prove the fact that an ink composition of the present invention comprising a copolymer (I) prepared by polymerizing a monomer mixture (I) containing methyl methacrylate, butyl acrylate and acrylic acid; and a copolymer (II) prepared by polymerizing a monomer mixture (II) containing styrene and maleic anhydride is more excellent than an ink composition comprising only one of the copolymer (I) and the copolymer (II).

#### EXPERIMENTS

The following experiments prove that an ink composition comprising the copolymer (I) and the copolymer (II) is more excellent than an ink composition comprising only one of the copolymer (I) and the copolymer (II) in storage stability for a long period of time, discharging stability and adhesion to printed matter at the same time.

#### PREPARATION EXAMPLE 1

Preparation of Dispersing resin (a) (copolymer (I))

A solution of 250 g of the monomer (A), 82 g of the monomer (B), 30 g of the monomer (C), 0.67 g of azobisisobutyronitrile and 350 g of benzene was added into a reaction container. After the atmosphere in the reaction container was substituted with nitrogen gas, the solution in the reaction container was subjected to thermal polymerization at 60°C for 7.5 hours with stirring to give a reactant.

After the reactant was dissolved in 3 L of methyl ethyl ketone to give a solution, the solution was precipitated with n-hexane in 7 times amount than the reactant to give a copolymer having the acid value based on carboxyl group of 65. After the copolymer was dried and ground, the ground copolymer was neutralized and dissolved with ammonia water in aqueous system to give Dispersing resin (a).

#### PREPARATION EXAMPLE 2

Preparation of Dispersing resin (b) (copolymer (II))

A solution of 225 g of the monomer (D), 132 g of the monomer (E), 0.54 g of azobisisobutyronitrile and 300 g of benzene was added into a reaction container. After the atmosphere in the reaction container was substituted with nitrogen gas, the solution in the reaction container was subjected to thermal polymerization at 70°C for 6.0 hours with stirring and continuously subjected to half-esterification with n-butanol to give a reactant. After the reactant was dissolved in 3 L of methyl ethyl ketone to give a solution, the solution was precipitated with n-hexane in 5 times amount than the reactant to give a copolymer having the acid value based on carboxyl group of 164. After the copolymer was dried and ground, the ground copolymer was neutralized and dissolved with monoethanolamine in aqueous system to give Dispersing resin (b).

#### PREPARATION EXAMPLE 3

Preparation of Dispersing resin (c) (copolymer (I))

A copolymer having the acid value based on carboxyl group of 110 was prepared in the same manner as in PREPARATION EXAMPLE 1 except that the amount of the monomer (C) was changed

from 30 g to 55 g. After the copolymer was dried and ground, the ground copolymer was neutralized and dissolved with ammonia water in aqueous system to give Dispersing resin (c).

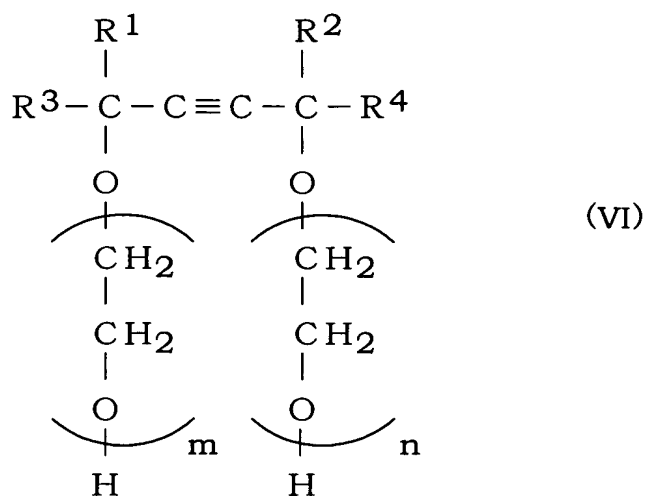
#### PREPARATION EXAMPLE 4

##### Preparation of Dispersing resin (d) (copolymer (II))

A copolymer having the acid value based on carboxyl group of 91 was prepared in the same manner as in PREPARATION EXAMPLE 2 except that the amount of the monomer (E) was changed from 132 g to 50 g. After the copolymer was dried and ground, the ground copolymer was neutralized and dissolved with monoethanolamine by using isopropanol as a dissolving auxiliary in aqueous system to give Dispersing resin (d).

#### EXPERIMENTS 1 to 3 and COMPARATIVE EXPERIMENTS 1 to 2

Pigment shown in TABLE 1 and a dispersing resin shown in TABLE 2 were mixed with each other and then, pure water was added thereto so that the content of the dispersed pigment was 25 % by weight to give a mixture solution. The mixture solution was dispersed with glass beads (diameter: 1.0 mm, amount: 1.5 times than mixture solution) for 2 hours in sand mill made by Yasukawa Seisakusho Kabushiki Kaisha. After the glass beads were removed from the mixture solution, thereto were added 20.0 % by weight of glycerin, 7.0 % by weight of maltitol, 2.0 % by weight of 2-pyrrolidon, 1.0 % by weight of the surface active agent (compound represented by the above formula (VI):



in which each of  $\text{R}^1$  and  $\text{R}^2$  was  $\text{CH}_3$ , each of  $\text{R}^3$  and  $\text{R}^4$  was  $\text{CH}_2\text{C}_2\text{H}_4\text{CH}_3$ , and the total of  $m$  and  $n$  was 10) and 0.9 % by weight of triethanolamine to give a mixture. Then, the mixture was stirred at ordinary temperature for 20 minutes. Finally, the mixture was filtrated with a membrane filter (pore size: 5  $\mu\text{m}$ ) to give a water-based ink composition for ink-jet printing.

The volume average particle size of dispersed pigment in the water-based ink composition for ink-jet printing was measured and the existence of coarse particles having a volume particle size of at least 500 nm was examined. The results are shown in TABLE 3.

TABLE 1

Experiment No.	Pigment	
	Kind	Content (% by weight)
1	Pigment Green 7	3.5
2	Pigment Green 7	3.5
3	Pigment Green 7	3.5
Com. Ex. No. 1	Pigment Green 7	3.5
2	Pigment Green 7	3.5

TABLE 2

Experiment No.	Dispersing resin			Content based on the amount of pigment (% by weight)
	Copolymer (I)	Copolymer (II)	(I)/(II) (weight ratio)	
1	Dispersing resin (a)	Dispersing resin (b)	67/33	35
2	Dispersing resin (c)	Dispersing resin (b)	67/33	30
3	Dispersing resin (a)	Dispersing resin (d)	67/33	30
Com. Ex. No. 1	Dispersing resin (a)	-	100/0	30
2	-	Dispersing resin (b)	0/100	30

### TEST EXAMPLES

Storage stability, discharging stability and adhesion of the water-based ink compositions for ink-jet printing prepared in EXPERIMENTS 1 to 3 and COMPARATIVE EXPERIMENTS 1 to 2 were examined in accordance with the following methods. The results are shown in TABLE 3.

#### (1) Storage stability of ink composition

The water-based ink composition for ink-jet printing was put in a sample bottle and allowed to stand in a thermostat at 70°C for 1 week.

Each viscosity of the ink composition before allowed to stand and after allowed to stand was measured by using ELD type viscometer. The difference between the viscosity before allowed to stand and the viscosity after allowed to stand was calculated, and storage stability of the ink composition was evaluated based on the following criteria for evaluation.

(Criteria for evaluation)

- A: The difference was less than 0.1 mPa·s.
- B: The difference was at least 0.1 mPa·s and less than 0.15 mPa·s.
- C: The difference was at least 0.15 mPa·s and less than 0.2 mPa·s.
- D: The difference was at least 0.2 mPa·s and less than 0.25 mPa·s.
- E: The difference was at least 0.25 mPa·s.

#### (2) Discharging stability of ink composition

An ink-jet printer (MJ8000C made by SEIKO EPSON CORPORATION) was charged with the water-based ink composition for ink-jet printing and then, 10000 sheets of printing paper (A4 size, fine



paper made by SEIKO EPSON CORPORATION) were subjected to printing in a usual manner at ordinary temperature. In the case that curve and/or lack on a printed matter due to blinding of nozzle generated during printing, the nozzle was subjected to cleaning. The number of cleaning was examined and discharging stability of the ink composition was evaluated based on the following criteria for evaluation.

(Criteria for evaluation)

A: The number of cleaning was less than 2.

B: The number of cleaning was at least 2 and less than 5.

C: The number of cleaning was at least 5 and less than 8.

D: The number of cleaning was at least 8 and less than 10.

E: The number of cleaning was at least 10.

(3) Adhesion of ink composition (Test of resistance for line marker)

Printing procedure by using the water-based ink composition for ink-jet printing was repeated in the same manner as in the above item (2) Discharging stability of ink composition. After the produced printed matter was dried for at least 1 day, the surface of the printed matter was rubbed with a water-based fluorescent pen (commercial name: ZEBRA PEN2 made by ZEBRA Co., Ltd., color: yellow) at a writing pressure of  $4.9 \times 10^5 \text{ N/m}^2$ . The existence of stain on the surface of the printed matter was examined and adhesion of the ink composition was evaluated based on the following criteria for evaluation.

(Criteria for evaluation)

A: There was no stain on the surface of the printed matter by rubbing one time.

B: There was a little stain on the surface of the printed matter by rubbing one time.

C: There was stain on the partial surface of the printed matter by rubbing one time.

D: There was stain on the whole surface of the printed matter by rubbing one time.

E: There was remarkable stain on the whole surface of the printed matter by rubbing one time.

TABLE 3

Water-based ink composition for ink-jet printing					
Experiment No.	Dispersed pigment		Property		
	Volume average particle size (nm)	Coarse particles	Storage stability	Discharging stability	Adhesion
1	131	None	A	A	A
2	127	None	B	B	A
3	178	None	B	B	B
Com. Ex. No. 1	210	None	B	C	A
2	125	None	D	B	E

From the results shown in TABLE 3, it can be understood that as to all water-based ink compositions for ink-jet printing prepared in EXPERIMENTS 1 to 3, the difference between the viscosity before allowed to stand and the viscosity after allowed to stand at 70°C for 1 week is less than 0.15 mPa·s, the number of cleaning is less than 5 during printing on 10000 sheets of paper and there is little stain on the surface of the printed matter by rubbing with the line marker. Accordingly, it can be understood that all water-based ink compositions for ink-jet printing prepared in EXPERIMENTS 1 to 3 are excellent in storage stability for a long period of time, discharging stability and adhesion to printed matter at the same time.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

This 8<sup>th</sup> day of April, 2003

by Kazuaki Watanabe

Kazuaki Watanabe

Minoru Waki

Minoru Waki

We, the undersigned witnesses, hereby acknowledge that Kazuaki Watanabe and Minoru Waki personally known to us and did execute the foregoing Declaration in our presence on:

Date: April 10, 2003

Witness Mahoto Matsumura

Date: April 9, 2003

Witness Airon Lan Pan